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14. ABSTRACT

Fluorinated polyhedral oligomeric silsesquioxanes (F-POSS), a subclass of POSS, were recently synthesized and have proven to be an excellent low-surface energy material for superhydrophobic and oleophobic surfaces. These F-POSS compounds consist of a silicon-oxide core with a periphery of long chain fluorinated alkyl groups ranging from 6-12 carbon atoms in length. Herein, a disilanol perfluoroalkyl polyhedral oligomeric silsequioxane (F-POSS-$(OH)_2$) has been synthesized *via* a viable multi-step synthesis (52% yield). These incompletely condesened structures were readily reacted with a variety of dichlorosilanes to produce functional F-POSS structures. Structures were confirmed with multinuclear NMR (^{1}H, ^{13}C, and ^{29}Si) and found to possess different solubility properties compared to the closed-cage F-POSS. These novel structures can be used as the initial building blocks for the development of new superhydrophobic and oleophobic materials.

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FUNCTIONAL PERFLUOROALKYL POLYHEDRAL OLIGOMERIC SILSESQUIOXANES (F-POSS): BUILDING BLOCKS FOR LOW SURFACE ENERGY MATERIALS

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Fluorinated polyhedral oligomeric silsesquioxanes (F-POSS), a subclass of POSS, were recently synthesized and have proven to be an excellent low-surface energy material for superhydrophobic and oleophobic surfaces. These F-POSS compounds consist of a silicon-oxide core with a periphery of long chain fluorinated alkyl groups ranging from 6-12 carbon atoms in length. Herein, a disilanol perfluoroalkyl polyhedral oligomeric silsesquioxane (F-POSS-$(OH)_2$) has been synthesized *via* a viable multi-step synthesis (52% yield). These incompletely condesened structures were readily reacted with a variety of dichlorosilanes to produce functional F-POSS structures. Structures were confirmed with multinuclear NMR (^{1}H, ^{13}C, and ^{29}Si) and found to possess different solubility properties compared to the closed-cage F-POSS. These novel structures can be used as the initial building blocks for the development of new superhydrophobic and oleophobic materials.

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Introduction

Polyhedral oligomeric silsesquioxanes (POSS), and their derivatives, have received much interest as a class of robust nanometer-sized building blocks for the development of high performance materials.[1-2] A fluorinated sub-class, consisting of a series of long-chain fluorinated polyhedral oligomeric silsesquioxane (F-POSS) compounds has recently been developed.[3-5] These F-POSS compounds consist of a silicon-oxide core with a periphery of long chain fluorinated alkyl groups ranging from 6-12 carbon atoms in length. These compounds have proven to be useful in the development and creation of low-surface energy materials.[6-9] Currently F-POSS is a standalone compound without any reactive chemical functionality. To circumvent the inert nature of these compounds, research has been performed on the functionalization of the $(trifluoropropyl)_7Si_7O_9(OH)_3$ with other long chain fluorinated compounds to produce low surface energy materials.[1] Although this synthetic strategy was successful, it was limited by the short length of the trifluoropropyl groups on the trisilanol. To date, there has been no viable synthetic strategy for functionalizable long-chain silanol F-POSS compounds.

Herein, using a similar synthetic strategy to that developed by Feher and coworkers, we report a procedure to synthesize incompletely condensed F-POSS cages.[10] A disilanol perfluoroalkyl polyhedral oligomeric silsesquioxane (F-POSS-$(OH)_2$) and its subsequent derivatives have been produced. This work represents the first functionalized long-chain F-POSS; these materials find applications in superhydrophobic/oleophobic coatings and low-surface energy materials.

Experimental

Materials. F-POSS (**1**) was synthesized using previously reported procedures.[5] All dichlorosilanes were purchased from Gelest and used without further purification unless otherwise noted. All reactions were performed under a nitrogen atmosphere unless otherwise noted.

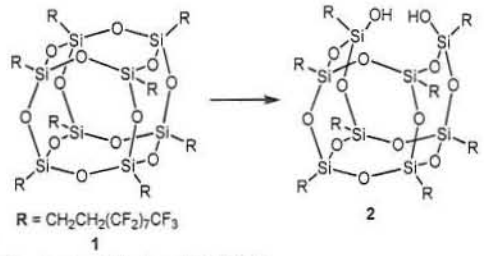
Instrumentation. ^1H, ^{13}C, and ^{29}Si NMR spectra were obtained on a Bruker 300-MHz or 400-MHz spectrometer. A heteronuclear inverse gated decoupling pulse sequence (NONOE) with a 12 sec delay was used to acquire ^{29}Si NMR spectra.

Synthesis of $(CF_3(CF_2)_7CH_2CH_2)_8Si_8O_{11}(OH)_2$ (2). Synthesis of compound **2** will be discussed in detail in future publications (52%). $^{29}Si\{^1H\}$ NMR (C_6F_6, 300 MHz) δ -59.2, -65.0, -68.2 (1:1:2). Anal. Calcd. for $C_{80}H_{34}F_{136}O_{13}Si_8$ (found): C, 23.94 (23.99), H, 0.85 (0.75), F, 64.44 (64.72).

General Synthesis of Functional F-POSS Compounds. $(CF_3(CF_2)_7CH_2CH_2)_8Si_8O_{11}(O_2Si((CH_2)_7CH_3)_2)$ (3). A solution of (3.0 g, 0.74 mmol), (**2**) di-*n*-octcadichlorosilane (0.255 g, 0.74 mmol) and NEt_3 (0.1 mL, 1.48 mmol) was stirred for 1 hour. During this time a white precipitate formed. This solution was filtered and poured into ethyl acetate, at which time, a white solid precipitated (**1**). This solid was removed *via* filtration and the filtrate was concentrated, then dissolved in diethyl ether and filtered. The filtrate was collected and cooled to 0 °C affording a white precipitate. The precipitate was collected and dried under vacuum to afford a white solid (**3**) (1.4 g, 44%). ^1H NMR (300 MHz, $(CD_3CD_2)_2O$, ppm) δ 2.24 (16H), 1.56-1.20 (32H), 5.87 1.15-1.5(18H) $^{29}Si\{^1H\}$ NMR (400 MHz, $(CD_3CD_2)_2O$, ppm) δ -17.8, -65.4, -68.2, -69.0 (1:2:4:2).

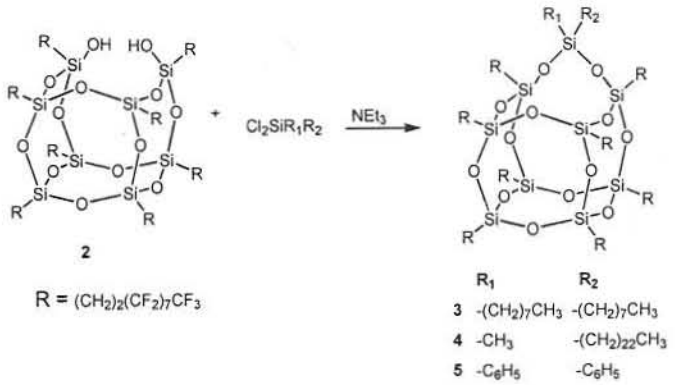
Results and Discussion

Synthesis of $(CF_3(CF_2)_7CH_2CH_2)_8Si_8O_{11}(OH)_2$. A multi-step reaction procedure was developed to convert the closed-cage F-POSS (**1**) to an incompletely condensed silsesquioxane structure (**2**). The first of these steps involves opening a single edge of the POSS structure with strong acid. The open edge is subsequently converted to a disilanol (*ca. 52%*) *via* a sulfate bridge and aqueous work-up. The main side product from each of these steps is compound **1**. Elemental analysis and ^{29}Si NMR were used to confirm the structure of **2**. The ^{29}Si NMR for compound **2** (-59.2, -65.0, -68.2) displayed a ^{29}Si chemical shift ratio of 1:1:2, which can be attributed to the *C2v* symmetry of the silsesquioxane (Figure 1). The peak at -58.7 is attributed to the silanols on the POSS structure. This provided evidence for an open cage structure.



Scheme 1. Synthesis of disilanol F-POSS.

Synthesis of $(CF_3(CF_2)_7CH_2CH_2)_8Si_8O_{11}(O_2Si(R_1)(R_2))$. The incompletely condensed silsesquioxane (**2**) can be readily reacted with a variety of dichlorosilanes (Scheme 2). The reaction of **2** with di-*n*-octcadichlorosilane in the presence of triethylamine produced compound **3** (ca. 44%). The main side product isolated during reaction was the initial starting material **1**. Multinuclear NMR (^1H, ^{29}Si) was used to confirm the structure of **3**. The ^{29}Si peaks were at -17.8, -65.4, -68.2, and -69.0, with a ratio of 1:2:4:2 (Figure 1). The peak at -17.8 ppm can be attributed to the Si with the dioctyl group attached. To demonstrate the robustness of the edge closing reaction other dichlorosilanes were reacted with **2** to produce compounds **4-5**. Dichorosilanes with alkyl and aromatic groups were chosen to evaluate the chemical robustness of **2**. All of these compounds were confirmed with multinuclear NMR (^1H, ^{29}Si).



Scheme 2. Synthesis of functionalized F-POSS.

Solubility of $(CF_3(CF_2)_7CH_2CH_2)Si_8O_{11}(O_2Si(R_1)(R_2))$ compounds. Although the large amount of fluorinated alkyl chains on **1** result in desirable properties and low surface energy, this also restricts the solvent choice for **1** to fluorinated solvents. Interestingly, once a non-fluorinated segment is added to an edge of F-POSS, the solubility properties of F-POSS change dramatically. For example, the long hydrocarbon chains present in compound **3** and **4** expand the F-POSS solubility to non-fluorinated solvents such as diethyl ether. Compound **4** demonstrated that unsymmetrical dichlorosilanes could easily be attached to a POSS cage. The long flexible chains for these molecules aided in rendering F-POSS soluble in non-fluorinated solvents. However groups such as a phenyl (**8**) were not able to improve the solubility of F-POSS. This can be attributed to the stiffness of the two phenyl groups on the POSS cage. We are currently developing other modified F-POSS structures.

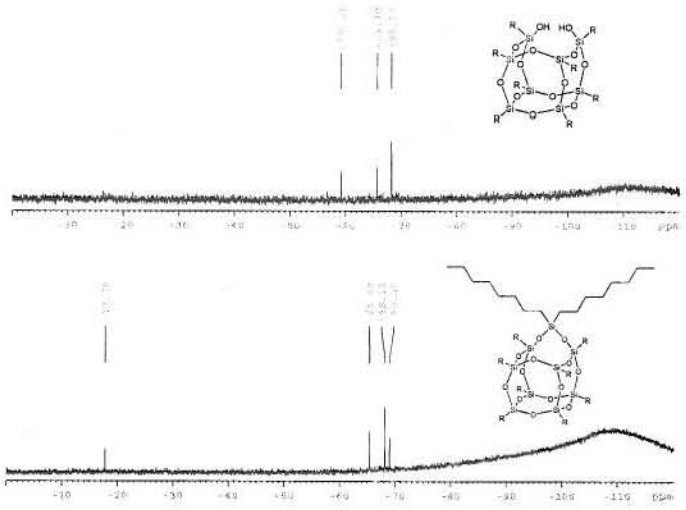


Figure 1. ^{29}Si *NMR of* **2** *(top), and* **3** *(bottom).*

Conclusions

The synthesis of disilanol F-POSS from F-POSS was accomplished in a three step reaction process. This incompletely condensed POSS structure was demonstrated to be reactive towards dichlorosilanes to produce a variety of functional F-POSS structures. These novel structures can be used as the initial building blocks for the development of new superhydrophobic and oleophobic materials.

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